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(54) PROCESS FOR THE PREPARATION OF ALKANONES FROM OLEFINS

(71) We, STAMICARBON N.V., a Netherlands Limited Liability Company of 2 van der Maesenstraat, Heerlan, the Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the preparation of alkanones e.g. acetone or butanone, from the corresponding olefins in the presence of a catalyst system comprising the oxides of molybdenum and tin supported on a thermostable carrier material.

Olefins can be converted into alkanones by oxidation over a catalyst as described hereafter. When the catalyst is still sufficiently active at low temperature, the selectivity favours the formation of alkanones. A disadvantage of a process in which a mixture of the olefin, steam, oxygen and, if desired, an inert gas is passed over a catalyst system comprising molybdenum oxide together with a tin oxide, supported on a thermostable carrier, is that for the formation of alkanones either the conversion or the selectivity is low. If the conversion of the olefin fraction on a single pass through the reactor remains below about 10%, an alkanone selectivity of for example 70% or higher can be achieved. At a higher conversion, however, the production of alkanones decreases and the production of carboxylic acids and carbon monoxide and carbon dioxide increases. For instance at a conversion of 90%, not more than 0.5% of the olefin is converted into alkanone, whereas 35% is converted into carboxylic acid and 55% into carbon monoxide and carbon dioxide.

It has now been discovered that if the catalyst as hereinbefore described is contacted alternately with gaseous streams as hereinafter described, the catalyst effectively becomes regenerated and the alkanone selectivity of the catalyst is enhanced.

The invention provides a process for the preparation of an alkanone from the corresponding olefin, which comprises contacting a catalyst system comprising the oxides of molybdenum and of tin supported on a thermostable carrier material; in which the said catalyst system is contacted alternately under reaction conditions of temperature and atmospheric and/or elevated pressure with two gaseous streams, one of the said gaseous streams containing the olefin to be converted and steam of and the other of the said streams containing oxygen but no olefin.

The gas mixture containing the olefin and steam should contain substantially no oxygen as the presence of oxygen has a deleterious effect on the reaction. In practice however it is not always possible to completely eliminate oxygen from the said steam, and preferably the said stream contains less than 0.5 parts by volume of oxygen per part by volume of olefin.

By controlling the temperature during the process of the invention so that the temperature does not rise excessively, the undue formation of carbon monoxide and carbon dioxide is avoided. However in these conditions reduction of the oxide components of the catalyst system is confined to the surface layer of the catalyst. Consequently unless extremely small catalytically active particles are present, only a small quantity of olefin can be oxidized per unit of volume of catalyst without the catalyst being contacted immediately with an oxygen-rich gas mixture. Thus under practical conditions, the catalytically active oxide particles should be as small as possible, and it is preferred that at least a major proportion of the oxide of tin is for the greater part present on the carrier material in the form of particles of at most 50Å.

Such a catalyst can be prepared by the homogeneous formation of hydroxyl ions, in a solution which contains tin ions and in which

a thermostable carrier material has been suspended, at a sufficiently gradual rate so that the concentration of metal-ions and hydroxyl-ions in the solution is at least approximately equal to the solubility product of the disposed insoluble metal oxide on the surface of the suspended carrier material, but insufficient to exceed the larger solubility product of nuclei of the oxide within the bulk of the solution. After precipitation of the tin compound a salt or oxide of molybdenum can be added to the suspension of the initially loaded carrier material, and the fully loaded carrier material is separated from the suspension, dried and calcined. The homogeneous and gradual formation of hydroxyl ions can be effected for example by the addition of urea to the suspension of the thermostable carrier material in the tin salt solution and by heating while stirring intensively the solution thus obtained so that the pH value of the solution increases very slowly, the heating being continued until the oxide has precipitated in the desired quantity on the carrier material.

In one embodiment of the process of the invention, the catalyst is stationary (i.e. in the form of a fixed bed) and is contacted alternately with the gas mixture containing the olefine to be converted and steam, and with an olefin-free gas mixture containing oxygen. This can be effected by periodically changing the composition of the reactor feed.

In another embodiment of the process of the invention, the catalyst itself is moved from one of the said gas streams to the other. Thus as in known processes for the catalytic cracking of petroleum fractions, the catalyst circulates between the reaction zone and a regeneration zone in a moving bed for instance in a fluidized state.

The process according to the invention results in the production of a gas mixture with a high content of alkanones, which may be from 5 to 20 times as high as in hitherto-known processes of the type in which a mixture of olefin, oxygen, steam and if so desired an inert gas is passed over the catalyst, and separation of the said alkanones is much easier than in such known processes.

The process is applied at atmospheric pressure or can be carried out entirely or partly at elevated pressure, for example up to 50 bar. The reaction temperature may be within wide limits for example between 150°C and 400°C. The contact of both the gas mixtures with the catalyst can each take place at a suitable pressure and temperature.

The olefin-free gas mixture used at atmospheric or slightly increased pressure is preferably air, and possibly containing steam.

When the process of the invention is carried out in the higher-pressure ranges, for example at 5 bar or higher, the use of technical oxygen, possibly together with steam, is preferred in order to avoid the introduction of nitrogen. Steam and/or an inert gas can be passed over the catalyst before and/or after the contacting with the olefin-free mixture.

The invention is hereafter more particularly described. In the run described a mixture of propane and steam, of n-butene and steam, and of air and steam were passed over a tin oxide/molybdenum oxide catalyst in a reactor under reaction conditions hereinafter described.

The preparation of catalysts "A" and "B" was effected as follows:

Preparation of tin oxide/molybdenum oxide catalysts on a silica carrier Catalyst "A"

2.25 kg of silica obtained under the Trade Mark AEROSIL and having a specific surface area of 200 m².g⁻¹, were suspended in a solution of 1.04 kg of SnCl₄.5 H₂O in 30 litres of water. 1.8 kg of urea were added after which the suspension was boiled while being strongly stirred, until the pH had increased from 0.5 to 2.2 over a period of time of 24 hours. The suspension was then cooled, the pH increasing further to 3. To the suspension thus obtained 0.6 kg of MoO₃ was added and the suspension stirred for another two hours. The solid material was then separated from the liquid by centrifuging, washed and dried. From the dried material cylindrical pellets containing 2% graphite were formed of 3 mm. length and 3 mm. square section. The pellets were calcined at 450°C, and steam was passed over for 16 hours at 450°C. By this procedure the extremely finely divided tin dioxide in the pellets was covered with a thin layer of molybdenum oxide. The composition of the final pelleted catalyst was 15% wt. SnO₂, 15% wt. MoO₃, 68% wt. SiO₂ and 2% wt. C. An electron-microscope revealed that tin dioxide particles with dimensions of about 30 Å had been deposited on the silica.

Catalyst "B"

Catalyst "B" was prepared by a similar procedure to catalyst "A", and had the composition 33.6% wt. SnO₂, 13% wt. MoO₃, 51% wt. SiO₂ and 2% wt. C.

Table I shows the results of the oxidation of propylene with catalyst "A", at a temperature of 260°C, atmospheric pressure and a space velocity of 127 vol/hour/vol.

The selectivity and conversion have been represented after the second step of this process had been carried out a number of times.

TABLE I

Oxidation of propylene Catalyst "A"

 $\text{C}_3\text{H}_6 : \text{H}_2\text{O} = 1 : 0.3$ (by vol); space velocity 127 vol/hour/vol
temp. 260°C

Time min.	Composition of end-product % mol			Conversion % mol
	CH_3CHO	CH_3COCH_3	CO_2	
5	0.1	99.9	0.00	14.2
18	0.05	99.95	0.00	11.6
26	0.05	99.95	0.00	9.05
34	0.05	99.95	0.00	6.7
42	0.02	99.98	0.00	5.35
50	0.02	99.98	0.00	4.45
58	0.00	100.0	0.00	3.55
66	0.00	100.0	0.00	3.0
74	0.00	100.0	0.00	2.5
82	0.00	100.0	0.00	2.3
30 min. regeneration with air + steam at 260°C (30 l of air and 8 l of H_2O per hour)				
5	0.10	99.9	0.00	13.3
18	0.10	99.9	0.00	11.4
26	0.05	99.95	0.00	8.75
33	0.05	99.95	0.00	7.85
41	0.05	99.95	0.00	5.65
48	0.02	99.98	0.00	4.3
80	0.02	99.98	0.00	2.3
15 min regeneration with air + steam at 260°C (30 l of air and 8 l of H_2O per hour)				
5	0.1	99.9	0.00	12.9
18	0.05	99.95	0.00	11.6
26	0.05	99.95	0.00	8.8
34	0.05	99.95	0.00	6.65

Tables II and III show the results of a comparative run (not according to the invention) of the oxidation of propylene and n-butene, respectively, corresponding to the first step of the process of the invention, carried out at a lower olefin/steam ratio 5

TABLE II

Oxidation of propylene Catalyst "B"

$C_3H_6 : H_2O = 1 : 2.2$ (by vol); space velocity 91 vol/hour/mol
temp. $257^\circ C$.

Time min.	Composition of end-product % mol			Conversion % mol
	CH_3CHO	CH_3COCH_3	CO_2	
9	0.1	99.9	0.00	42.2
18	0.1	99.9	0.00	37.0
20	0.1	99.9	0.00	28.1
22	0.1	99.9	0.00	25.4
30	0.05	99.95	0.00	19.1
32	0.05	99.95	0.00	18.1
34	0.05	99.95	0.00	15.9

TABLE III

Oxidation of n-butene Catalyst "B"

$C_4H_8 : H_2O = 1 : 2.2$ (by vol.); space velocity 91 vol/hour/mol
temp. $253^\circ C$.

Time min.	Composition of end-product % mol				Conversion % mol
	CH_3CHO	CH_3COCH_3	$CH_3COCH_2CH_3$	CO_2	
13	0.1	2.0	96.7	1.0	21.3
21	0.1	1.1	97.8	0.7	16.4
29	0.05	0.9	98.1	0.8	15.1
37	0.05	0.8	98.1	1.0	11.4
45	0.05	0.7	97.9	1.3	9.1

Figure 1 of the accompanying drawings is a graph showing the conversion as a function of the reaction time, for different space velocities. The abscissa is time in minutes and the ordinate is conversion in mol. %. The curves A, B and C relate to the preparation of acetone from propylene at space velocities of 170, 91 and 39 vol/hour/vol respectively, and curve D refers to the preparation of butanone from n-butenes at a space velocity of 91 vol/hour/vol. For these runs Catalyst "B" was used. The catalyst bed was kept at a temperature of 257°C, whilst the olefin/steam volume ratio used was 1:2.2. The selectivity for the formation of acetone from propylene was 99.9%, and for the formation of butanone from butene about 95%. From the graph it is apparent that the conversion decreases at higher space velocities, and furthermore at a given space velocity the conversion of butene was lower than that of propylene.

The graph of Figure 2 of the accompanying drawings represents the effect of the temperature of the catalyst bed. The abscissa is time in minutes and the ordinate is conversion in mol. %. This graph shows exclusively the preparation of acetone from propylene. The reaction temperatures applied are indicated on the relevant curves. For these runs Catalyst "A" was used. The propylene/steam volume ratio was 1:0.3 and the space velocity was 127 vol/hour/vol. The selectivity for the formation of acetone was 99.9%. As is apparent from the graph, the temperature at which the reaction is carried out had only a slight influence on the progress of the conversion in relation to time.

The ratio of the concentrations of olefin and oxygen in the stage of the process according to the invention in which a gas mixture comprising olefin and steam and is used strongly influences the selectivity for the formation of alkanones. The graphs shown in Figures 3 and 4 of the accompanying drawings show selectivity as a function of the oxygen/olefin ratio under the conditions indicated in the graphs, of which the abscissa is the oxygen partial pressure in bar and the ordinate is the selectivity per cent. For these runs catalyst "A" was used. In the runs of Figure 3 the space velocity was 1950 vol/hour/vol, in those of Figure 4 it was 890 vol/hour/vol. In the runs of Figure 3 the propylene and steam partial pressures used were 0.050 and 0.25 bar, respectively, in those of Figure 4 the butene and steam partial pressures used were 0.027 and 0.284 bar, respectively. The excess of steam in these runs was higher than that in the runs according to Tables I, II and III. It is clearly apparent that the selectivity decreases strongly with an increasing oxygen/olefin ratio, this applies in particular to the preparation of butanone from butenes.

These runs illustrate the necessity for the

olefin steam to be substantially oxygen-free, i.e. containing no oxygen or preferably less than 0.5 parts by volume of oxygen based on the olefin component.

Having regard to the provisions of Section 9 of the Patent Act, attention is directed to the claims of Patents Nos. 1,240,858, 1,213,520 and 990,639.

WHAT WE CLAIM IS:—

1. A process for the preparation of an alkanone from the corresponding olefin which comprises contacting a catalyst system comprising the oxides of molybdenum and of tin supported on a thermostable carrier material alternately under reaction conditions of temperature and atmospheric and/or elevated pressure with two gaseous streams, one of the said gaseous streams containing the olefin to be converted and steam and the other of the said streams comprising a gas mixture containing oxygen but no olefin.
2. A process according to Claim 1 wherein the said gaseous stream containing olefin and steam contains less than 0.5 parts by volume of oxygen per part by volume of olefin.
3. A process according to Claim 1 or Claim 2, wherein the said olefin-free stream is air and possibly contains steam.
4. A process according to Claim 1 or Claim 2, wherein the said olefin-free stream contains oxygen of technical grade and possibly contains steam.
5. A process according to any of Claims 1 to 4, wherein the process is carried out at a pressure of at least 5 bar.
6. A process according to any of Claims 1 to 5, wherein the process is carried out at a temperature in the range 150° to 400°C.
7. A process according to any of Claims 1 to 6, wherein the oxide of tin is in the form of particles of size not more than 50 Å.
8. A process according to any of Claims 1 to 7 for the preparation of acetone from propylene.
9. A process according to any of Claims 1 to 7 for the preparation of butanone from n-butenes.
10. A process according to any of Claims 1 to 9, wherein the catalyst system is in the form of a fixed bed in a reactor.
11. A process according to any of Claims 1 to 9, wherein the catalyst system is in the form of a moving bed.
12. A process according to Claim 11, wherein the said moving bed is a fluidized bed.
13. A process according to Claim 11 or Claim 12, wherein the said catalyst system circulates between a reactor zone and a regeneration zone.
14. A process for the preparation of alkanones according to Claim 1, substantially as hereinbefore described.
15. Alkanones prepared according to a process as claimed in any of Claims 1 to 14.

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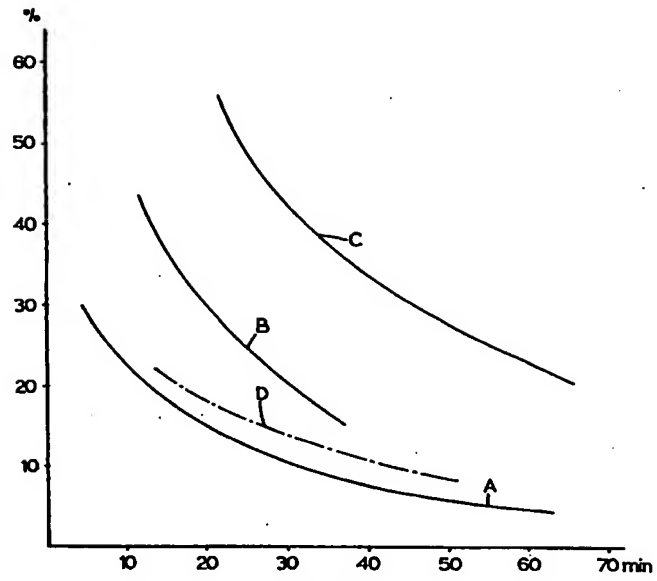


FIG.1

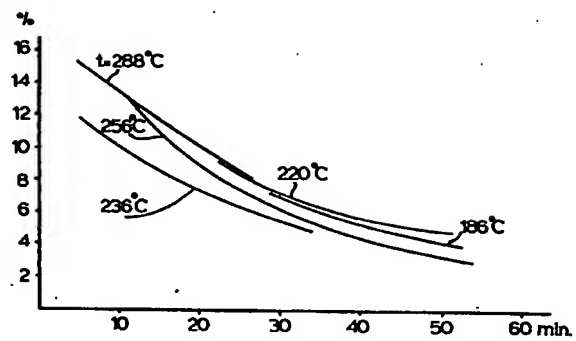


FIG.2

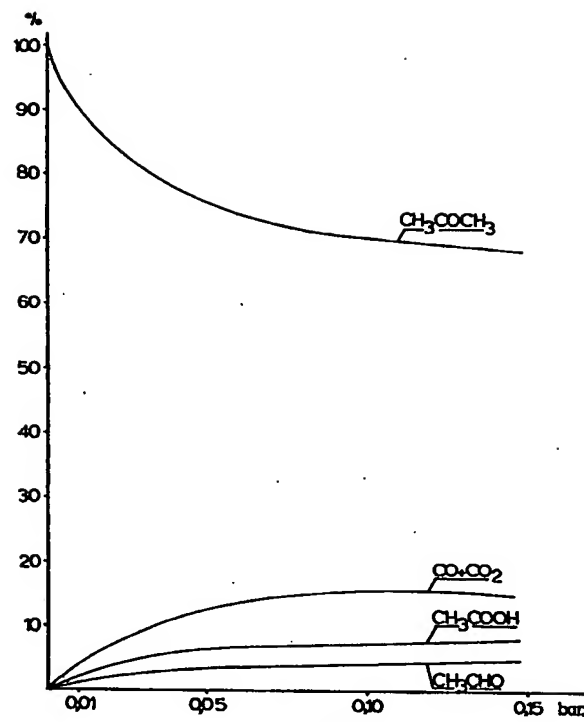


FIG.3

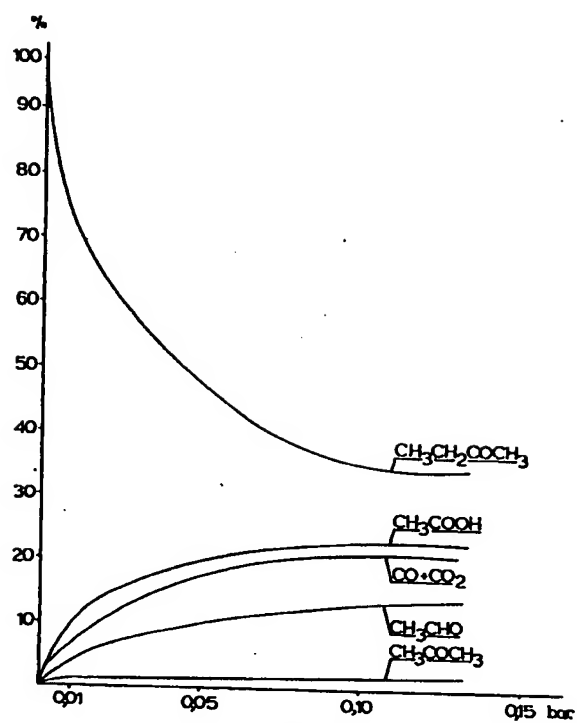


FIG.4